Figures

Appendices

SECTION 6   DETERMINING THE CORRECTIVE ACTION STANDARD

Criteria for determining allowable COC residuals are based on risk assessment and regulatory requirements. Once established, these levels of COCs represent the concentrations that may be left in place and be protective of human health and the environment. For LUST sites, these corrective action standards are determined using a tiered evaluation process. This risk-based tiered procedure is described in the following sections. Basic elements of risk assessment methodology and the tiered procedure for determining risk-based corrective actions are discussed in Section 6.1. Sections 6.2 through 6.4 present detailed information for each of the three tiered evaluations used in determining the corrective action standard.

6.1   BASIC ELEMENTS OF THE TIERED PROCEDURE FOR DETERMINING RISK-BASED CORRECTIVE ACTIONS (RBCA)

In determining the appropriate risk-based cleanup standard for a LUST site, an evaluation is conducted of the levels of contaminants in environmental media, the distribution and migration pathways of these contaminants at the site, the human or environmental receptors which may come into contact with contamination, and the routes of contact which may occur between receptors and contaminants. As described in Section 4.1.3, this information is developed during site investigation activities and is used in constructing a CSM. The CSM serves as a tool for identifying the scenarios which should be evaluated for potential impacts to human health and the environment.

It will become evident, upon review of the tiered evaluation sections, that the CSM reflects the level of development of site-specific information. This site-specific information summarized in the CSM is the same information that is used in the tier evaluation process to better define those COCs which require a remedial response and the level of COCs which constitute the risk -based corrective action standard. At Tier 1, all pathways are considered to be complete for all COCs detected at the site. Therefore, the CSM conservatively assumes types of exposure or levels of exposure which may not currently exist. This results in a risk-based corrective action standard which is protective of the CSM assumed conditions, rather than site-specific conditions. At Tier 2, additional information is analyzed to selectively eliminate COCs or exposure pathways from further evaluation. Here, the CSM corresponds more closely with the site-specific information used to determine a site-specific risk-based corrective action standard.

The following sections discuss the basic components used in the development of the tiered process for determining the risk-based corrective action standard.

6.1.1 Receptors

The evaluation of risk from site-related COCs is based on a general or site-specific exposure scenario, which identifies activities occurring at the site and uses of the property relative to specific receptors having access to the site. The following is a description of receptors to be evaluated for the categories of exposure scenarios which may be applicable for a given site :

Residential: Typically a location where someone is present for an average of more than 8 hours a day. It includes, but is not limited to, schools, dwellings, residences, hospitals, child care centers, nursing homes, correctional facilities, and any other human activity areas of repeated, frequent use and/or chronic duration.

Construction: Typically, locations where construction activities are underway for a substantial period of time, *e.g.* months to years, resulting in sub-chronic exposures for on-site construction workers for only that period equal to the duration of the project.

Non-residential: Typically a location where someone is on-site an average of 8 hours a day, a typical work day. It includes, but is not limited to, all types of commercial and industrial operations, such gas stations, dry cleaners, airports, marinas, municipal and military motor pools, trucking maintenance and refueling terminals, and commercial agricultural operations. This non-residential category may further be refined into commercial or industrial uses. These are locations where employees work, but do not reside on a continuing basis. Hotels, motels, and other **transient** activities are included in the non-residential definition, rather than as residential.

Recreational: Typically a location of intermittent and variable uses dependent upon the natural and man-made features present, and the geographical location. Therefore, the receptor uses and behavior patterns in this exposure scenario are highly site-specific. These locations include parks, playgrounds, golf courses, camping grounds, waters of the state with permitted uses, hiking areas, etc.

Off-Site Receptors: Land use and receptors within ¼ mile of the site should be surveyed. Where contaminant plumes extend or are likely to extend beyond ¼ mile of the property boundary, land use and receptors in those areas should be included in the receptor survey.

The categories of land use adjacent to the site should be clearly identified and labeled on the site plan submitted with the RBCA tier evaluation.

If future land use is likely to be substantially different than current land use, this should be reflected in the CSM and in the tier evaluation. This is particularly important when property use is likely to change prior to closure of the LUST case. This information should be supported by documentation, such as trends in zoning changes for the locale, urban planning commission reports, or purchaser agreements, when available.

6.1.2 Chemicals of Concern

For purposes of the UST Program, chemicals of concern (COCs) are those substances contained within a regulated UST system that have been released into environmental media. In practical terms, these regulated substances can be detected and reported when environmental samples are analyzed by a laboratory. It is these COCs that are subject to delineation in the course of the investigation at the LUST site. Upon site characterization, these COCs are evaluated for their potential impacts to public health and the environment. Only selected COCs may be present at levels at the LUST site which warrant remedial action or evaluation beyond the screening level Tier 1. COCs which may be subject to further evaluation or remedial action occur at concentrations exceeding the lower threshold of the applicable pre-determined SRL, MCL, minimum GPL, surface water quality standard, or other conservative benchmark.

The selection of COCs pertaining to a potential petroleum hydrocarbon release are based upon site history and the analytical results from a release confirmation. The subsequent LUST site characterization should include analyses for fuel hydrocarbons (volatile and extractable), BTEX (benzene; toluene; ethylbenzene; and ortho-, meta-, and para-xylenes), PAHs (polycyclic aromatic hydrocarbons), and MTBE (methyl tertiary-butyl ether) where applicable. Infrequently, analysis for heavy metals, lead scavengers, or fuel additives may be necessary. Analysis for TPH fractions, as described below, should be conducted to support evaluation of the non-cancer hazard to humans. These analytes are consistent with the hydrocarbon products in USTs, and provide indicators for the chemicals of concern (COCs) that

should be part of a risk-based confirmation of successful remedial action for site restoration.

Nominally, the COCs should include:

• BTEX

Benzene is an indicator chemical for carcinogenic effects of low-molecular weight hydrocarbons. Toluene, ethylbenzene, and xylenes are non-carcinogens with less stringent risk-based concentrations. BTEX is especially important for corrective action involving gasoline releases at LUST sites.

• Petroleum Hydrocarbons

TPH fractions should be included in site characterization. The range of effective carbon chain length and relative percentage composition is characteristic for specific types of neat petroleum products. However, once released into the environment, these hydrocarbon patterns are subject to change from process of weathering and decomposition. Yet, hydrocarbon analysis provides useful information regarding the potential presence and levels of single chemical constituents. It may also be evaluated for potential impacts to human health and the environment as a chemical mixture.

• MTBE

Unless the site history and materials usage records support the absence of MTBE, analyses of samples for gasoline storage facilities must include MTBE as an analyte.

• PAHs

Polycyclic aromatic hydrocarbons (also called, polynuclear aromatic hydrocarbons, PNAs) should be COCs for delineation and confirmation of site remediation. Since PAHs are typically recalcitrant to biodegradation, their ultimate fate in bioremediation has greater uncertainty, and they should be confirmed specifically. Benzo(a)pyrene is especially important as an indicator chemical for cancer effects of heavy petroleum hydrocarbons fractions, and petroleum products which have undergone sustained conditons of heat and pressure from mechanical frictional wear or combustion processes.

• Lead Scavengers

Leaded gasoline fuels contains additives known as organolead compounds. These lead compounds, i.e., tetraethyllead, tetramethyllead, trimethyllead, dimethyllead, and methyltriethyllead, required the presence of lead

scavengers to prevent engine deposits of the lead oxide combustion product. These lead scavenger compounds are ethylene dichloride (1,2-DCA, also known as 1,2-dichloroethane) and ethylene dibromide (EDB). The amount of added 1,2-DCA or EDB is proportional to the amount of organolead in fuel. Once released into the environment, 1,2-DCA and EDB are typically resistant to chemical and biological degradation, causing them to be relatively persistent. Due to their chemical and physical properties, these compounds volatilize quickly withing the vadose zone, dissolve quickly into the aqueous phase in the saturated zone of the subsurface, or remain within free product when present. Therefore, unless the release can be documented to occur prior to or during the phase out period of leaded fuels for automobiles in Arizona or unless the release involves leaded aviation fuel, lead scavengers would not be regarded as COCs at a LUST site.

6.1.3 Site Conditions

Information regarding site conditions must be developed to support the conceptual understanding of the site and to provide the proper basis for the quantitative evaluation of risk/hazard. The guidance on land use activity type in Section 6.1.1 also applies here. The description of site conditions is embodied in and is implied by the designated exposure pathways in the CSM. For instance, with reference to Figures 4.1.3.a and 4.1.3.b, a site with no surface water associated with it would show an incomplete pathway for surface water. A site with commercial-industrial land use would show adult worker receptors on-site, but no children receptors (unless there is a site-specific peculiarity whereby children would be present). Conditons at a site, where a remedial action has already been taken or where institutional controls have eliminated certain exposures, can be so noted on the CSM using the number notations ($\hat{I}$ - $\grave{O}$) as in Figure 4.1.3.a. Of course, existing institutional or engineering controls are not sufficient to designate an incomplete pathway for future exposure scenarios, if the presence or maintenance of those controls are not guaranteed and memorialized by a Declaration of Environmental Use Restriction [DEUR, A.R.S. § 49-152(B)].

Conditions at the adjacent properties may also need to be evaluated relative to the LUST site **in instances when the LUST site is a commercial or industrial property which is surrounded by residential development**. One aspect is the future potential impacts resulting from contaminants migrating beyond the property boundary. An evaluation of off-site migration potential and contaminant exposure point concentrations should be conducted for residential use scenarios, and should be provided in a CAP.

The other aspect is that of future property use changes of the commercial or industrial property to that of the surrounding property uses, *i.e.*, residential. If contaminated media at the LUST site will not be remediated to residential levels, a guarantee must be provided that the site will remain commercial or industrial in the future through the implementation of the non-residential use restriction DEUR.

Another important aspect of site conditions is geotechnical characterization of the subsurface conditions. In particular, measurement of a few soil parameters during initial mobilization for site characterization is relatively cheap and can provide significant benefit in the site-specific results of the Tier 2 evaluation, if required. The parameters are **1) average fraction of organic carbon, 2) dry soil bulk density, and 3) average soil moisture**. These geotechnical parameters have higher sensitivity than other geotechncial parameters in the fate and transport equations useful for site-specific conditions in Tier 2. As this is a general overview of the elements of the tiered RBCA process, further detail on geotechnical conditions is provided in Section 6.3.

6.1.4 Representative Soil, Groundwater and Surface Water Concentrations

If there were one magic concentration for each COC and environmental medium that is "representative" of the site, numerical evaluation would be relatively simple for decision making. Because environmental releases are, by definition, concentrations above background, the extent of a release is determined by establishing its boundary. The **investigative** COC concentrations for vertical and lateral delineation are not necessarily the same as the **representative** exposure point concentration in a given environmental media which is evaluated for impacts to human health and the environment. For LUST releases, the vertical boundary of the release is where the COC concentrations do not exceed laboratory reporting levels. However, the lateral boundary is the lesser of the applicable protective criteria of the State of Arizona, or those concentrations which do not present a significant risk/hazard to human health. This implies that risk-based criteria or ADEQ promulgated criteria can be used to delineate a plume in either soil or groundwater. The plume, thus delineated, can be designated an area of concern (AOC, see Glossary for definition). This has significant implications for how site characterization data may be used.

6.1.5 Overview of Fate and Transport of Contaminants

The fate and transport of COCs are important factors for site characterization, risk assessment, remediation, and site restoration. The potential pathways of migration in the environment and routes of human exposure are determined by the physical and chemical properties of chemicals released.

6.1.5.1 Potential Routes of Migration

The initial conceptual model indicates that chemicals released into the environment might be released to the air by volatilization or wind suspension of dust and could result in inhalation exposures for workers at the site or future potential human receptors. Humans could be exposed to chemicals in soil via release to the atmosphere, direct contact with the skin, or incidental ingestion. Chemicals in soil can also be transported in surface-water runoff and sediments and might percolate to groundwater. Although exposures to surface-water runoff and sediments are not considered likely at most Arizona UST sites, exposure to chemicals in groundwater by inhalation, ingestion, and dermal contact absorption must be included in the Tier 1 evaluation.

For the groundwater and soil samples collected during site characterization, information on the properties of the COCs and their behavior in the environment must be addressed in the risk-based evaluation. Information on the behavior of petroleum and BTEX COCs in the environment may be obtained from the ASTM standard guide (1995). Additional sources of similar information are the Hazardous Substances Data Bank (HSDB, http://chem.sis.nim.nih.gov/hsdb) compiled by the National Library of Medicine and the reports by Howard, *et al*, 1989, 1990, 1991a, 1991b).

6.1.5.2 Contaminant Persistence

Organic contaminants identified in environmental media are thermodynamically unstable and will tend to degrade with the time in the natural environment. Metals may persist without change in the environment or may be transformed via biotransformation, oxidation, or complex formation. Sorption or chemical speciation processes may also affect environmental disposition.

Chemicals that might degrade rapidly to nonhazardous products usually represent a lesser hazard to human health and the environment than more

persistent chemicals. Intermediate degradation products may include other hazardous compounds. For instance, *n*-hexane partially oxidizes to 2,5-hexanediol and 2,5-hexanedione, which has higher toxicity than *n*-hexane. However, given enough time, these compounds eventually will decompose completely to carbon dioxide and water. The persistence of these contaminants depends on the rates of these degradation processes and is usually limited by the microbial degradation (biodegradation) rate.

Degradation of chemicals in soil and water is usually dominated by biodegradation mechanisms, with the exception of those that undergo rapid hydrolysis reactions. A variety of abiotic processes are also important for certain classes of compounds. The effective degradation rate of a specific chemical is described in terms of the degradation half-life. This factor is important to evaluate when assessing the potential range of COCs in site-specific future exposure scenarios.

<u>Biodegradation</u>
Biodegradation results from the action of microorganisms on the chemical. Degradation of chemicals in soils is usually dominated by biodegradation processes. Degradation of chemicals in surface water is dominated by biodegradation, with the exception of those degraded by photolysis and photooxidation reactions. Biodegradation also is predominant in groundwater, although at slower rates than in surface water (Howard, et al., 1991). In general, aerobic biodgradation of halogenated chemicals is slower than for alcohols or carboxylic acids.

Factors affecting biodegradation rates of contaminants in soil and groundwater included pH, dissolved oxygen concentration, availability of macro and trace nutrients, and temperature. Without measuring these site-specific conditions in environmental media at the LUST site, quantitative rates cannot be determined. However, numerous studies have been completed on the degradation rates of chemicals in a variety of different environments. These studies provide an approximate range of degradation rates for specific contaminants in various environments. These published degradation rates may be used in a screening level evaluation of biodegradation for the site to determine if the use of biodegradation is feasible for addressing contaminant levels at the site, and supports the collection of site-specific data. Care should be taken to utilize those literature values which are most similar to conditions at the site to the extent available.

<u>Abiotic Degradation</u>

Abiotic degradation processes include hydrolysis, photolysis, and photooxidation. In water, abiotic degradation often results from hydrolysis, depending on the pH of the water at the site. Hydrolysis can occur more rapidly than biodegradation and is the predominant degradation mechanism for classes of chemicals that can undergo rapid hydrolysis reactions, such as esters and aliphatic halogens (Howard et al., 1991). Photodegradation is the predominant process in air for those chemicals with permissive spectral properties.

Factors affecting abiotic degradation rates of contaminants in soil and groundwater include the spectral properties of the chemical (for chemicals in surface soil and water), light intensity, dissociation constant (pK_a), oxidation potential, and temperature.

Bioconcentration

Bioconcentration factors (BCFs) are used to describe the tendency of a chemical to accumulate in aquatic organisms. Hydrophobic compounds can accumulate in biolgical systems to potentially toxic concentrations and contribute to the food chain. Bioconcentration associated with UST sites is usually linked to higher molecular weight TPH and is not usually associated with USTs containing gasoline and diesel fuel.

6.1.5.3   Contaminant Migration and Chemical Properties

Chemicals that have properties   preferential for evaporation into air, dissolution in water, or concentration in plants will have different routes of exposure to humans. Migration of chemicals released into the environment is governed by the properties of the chemical in question and the properties of the site. Important properties of the site are climatic factors, such as ambient temperature and wind, and chemical properties of soil and water. The pH of water and the organic carbon content of soil at the site are particularly important.

The chemical properties affecting contaminant migration include solubility, dissociation constant, octanol/water partition coefficient, soil or sediment partition coefficient, Henry's Law constant, and vapor pressure. The chemical and physical characteristics that influence the mobility and biological availability of these chemicals are summarized in ASTM (1995).

6.1.6 Exposure Pathways

An exposure pathway describes the course a chemical or other exposure agent takes from the source to the exposed individual. An exposure pathway analysis links the sources, locations, and types of environmental releases with population locations and activity patterns to determine the significant pathways of human exposure. A cartoon depiction of typical exposure pathways is shown in Figure 6.1.6.a. The pathways indicated can also be found in the CSMs of Figures 4.1.3.a and 4.1.3.b.
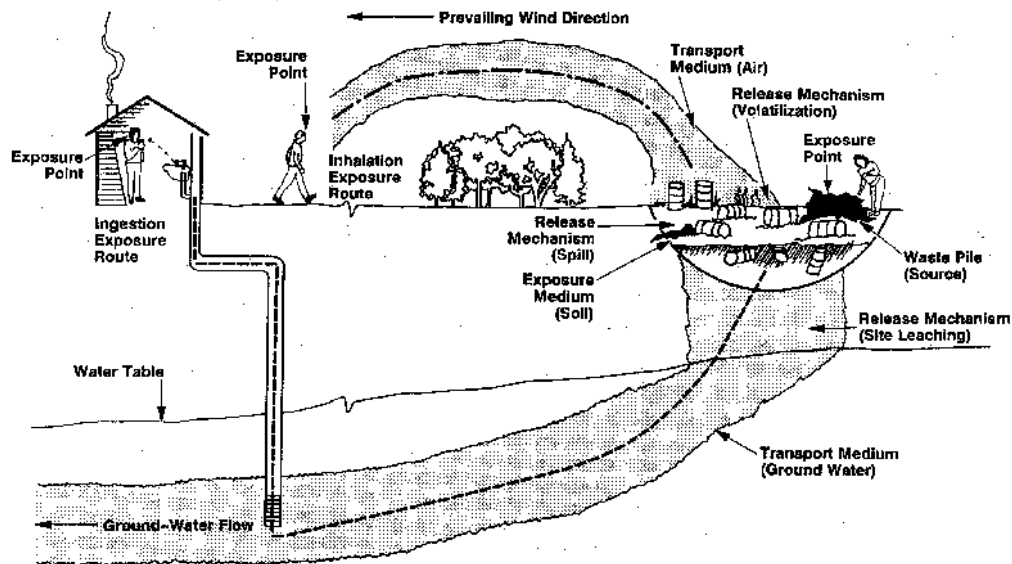
Figure 6.1.6.a Exposure Pathways (from RAGS, EPA, 1989a).

6.1.7 Point of Exposure

A point of exposure is a location where contact with contaminated media occur. In some cases, the primary release itself (*e.g.*, contaminated soil from a UST release) is the exposure point, without a release to any other medium. In other cases, there may be a secondary release from contaminated soil with leaching to groundwater or volatilization to enclosed or ambient air. All of these releases, primary and secondary, can result in COC exposures to a receptor at a particular location . Exposure at a particular locaction leads to an exposure route where entry into the body can occur. Figure 6.1.6.a illustrates the importance of location to the mode of exposure, *i.e.* ingestion, dermal contact absorption, or inhalation, and the concentrations of the COCs at the point of exposure.

6.1.8 Overview of Toxicology

This section provides a very brief discussion of toxicology and its use in evaluating health impacts resulting from environmental exposures to chemicals. The interested reader will also find useful information in EPA, 1989a, Chapter 7; Casarett and Doull's Toxicology, 1986; and the Toxicology Tutor of the National Library of Medicine at http://sis.nlm.nih.gov/toxtutor.cfm. A more detailed discussion is provided in Appendix O.

Data from toxicity studies provide the basis for characterizing potential health impacts from exposures resulting from a release into the environment. Information collected during site characterization and the chemical properties of COCs at the site are evaluated to construct an **Exposure Assessment** consisting of an exposure scenario, a receptor population, and construction of an exposure dose. The exposure dose is compared to toxicity reference information from a **Toxicity Assessment** to prepare a **Risk Characterization** for risk assessment and subsequent risk management.

The toxicity endpoints for a particular chemical would be either carcinogenesis (benzene, for example) or systemic poisoning (benzene, non-cancer endpoint, or toluene, a non-carcinogen, as examples). With the current state of knowledge, toxicity standards are being compiled for oral and inhalation exposure pathways. The oral toxicity standard is used to approximate the dermal toxicity standard in risk-based evaluation.

For chemicals with systemic effects, the toxicity is defined by the reference dose (RfD). The reference dose is an estimate, incorporating a level of uncertainty spanning perhaps an order of magnitude or greater, of a daily exposure level for the human population, including sensitive sub-populations, that is likely to be without an appreciable risk of deleterious effects during a lifetime (EPA, 1989a, page 7-5). Chemical-specific reference doses are listed in EPA's Integrated Risk Information System (IRIS; http://www.epa.gov/ngispgm3/iris/index.html).

For chemicals with carcinogenic effects, the toxicity is defined by the weight of evidence classification and the carcinogenic slope factor (SF). EPA evaluates the data available supporting the carcinogenic effects of a chemical. The classification system of weight-of-evidence for carcinogenicity has been developed and is listed as shown below.

EPA's Weight-of-Evidence Classification System for Carcinogenicity*	
Group	**Description**
A	Human carcinogen
B1 or B2	Probably human carcinogen
	B1 indicates that limited human data are available. B2 indicates sufficient evidence in animals and inadequate or no evidence in humans
C	Possible human carcinogen
D	Not classifiable as to human carcinogencity
E	Evidence of noncarcinogenicity for humans
*EPA, 1989a, page 7-11.	

At LUST sites, benzene, a group A carcinogen, is the driver for risk assessment of a relatively fresh gasoline release. For other petroleum releases, PAHs might be involved. Some PAHs are non-carcinogens, but several have carcinogenic effects. The question of whether the risk for PAHs and benzene should be summed in a risk assessment is based on the weight-of-evidence classification. In general, risks from weight-of-evidence classes A and B (and C where slope factors exist for those chemicals) should be summed. EPA's proposed revisions to the cancer assessment guidelines in 1996 [http://www.epa.gov/neca/cancer.html] will change this approach to evaluating carcinogenicity. Upon publication, this guidance will be revised accordingly.

Toxicity factors for carcinogens are expressed by the relationship between the dose and the response and is referred to as the slope factor, which is the slope, **m**, of the line defining the dose-response relationship. The slope factor has units of $(mg/kg\text{-}day)^{-1}$. It represents an upper 95th percent confidence limit on the probability of a response per unit intake of a chemical over a lifetime (EPA, 1989a, page 7-12). The slope factors with their respective weight-of-evidence groups and the source of the data must be tabulated in the corrective action risk assessment for closure.

When a chemical present at a LUST site does not have an EPA provided toxicity factor, proposal of alternate or provisional toxicological factors should be done in conjunction with the ADEQ risk assessor.

Other modifications to exposure and toxicity evaluations made be made but should be done at the level of Tier 2 or Tier 3 evaluations. These include exposure evaluations for exposures occurring by pathways other than ingestion, inhalation, and dermal contact with contaminated environmental media. This is the case, for example, when crops grown on the site or fish raised in contaminated water on the site are ingested.

Modifications may also be applied to absorbed dose parameters. For example, the amount of a chemical in environmental media, to which a receptor is exposed, is not the same as the amount of chemical which is actually absorbed and linked to exposure effects. However, this assumption is made unless data is provided as justification, as part of a Tier 2 or Tier 3 evaluation. An example is for chemical-specific permeability coefficients, K_p's, used in assessing dermal toxicity. These may be modified, with justification, in Tiers 2 and 3.

When exposure and toxicity assessments need to account for receptor exposures other than continual and chronic in duration, alternative toxicity standards are available. In general, the shorter the exposure time, the higher is the allowable dose. EPA's Office of Drinking Water has developed One- and Ten-day Health Advisories for drinking water intake (*http://www.epa.gov/ost/drinking/standards*). While they are nonregulatory guidance, they serve a useful purpose for site-specific conditions where concentrations are greater than risk-based drinking water PRGs, GPLs, or AWQLs. Short-term criteria can be useful in indicating a more immediate threat that should be addressed through an interim remedial action that will protect human health and allow a more systematic approach to corrective action and final closure of the site. Site-specific evaluation for corrective action planning should always include a screening level evaluation to see if there are immediate threats that should be addressed before the planned corrective action. In such cases, communication with the ADEQ case manager for the site must be maintained to ensure that site-specific changes are known to all the stakeholders.

6.2 Tier 1 Evaluation

The Tier 1 evaluation is the most conservative, protective evaluation of the three tiers. It is based on the highest and best use of the site as either residential or non-

residential. All exposure pathways are considered to be complete for all contaminated media. The Tier 1 evaluation is applied to all sites as a conservative screening level evaluation for decision making on closure, remedial action, or further site evaluation.

6.2.1 Tier 1 Corrective Action Standards

Essentially, there are two types of Tier 1 standards. One consists of those "enforceable" regulatory numbers which have been calculated by some defined method, and are adopted or promulgated under existing Arizona statute or rule. The other type consists of those "recommended" numbers which are calculated by similar methods or alternative methods, but do not exist as a fixed numerical value under rule or statute. These "recommended" Tier 1 numbers, also serve to protect human health and the environment.

For contaminated soil exposures, the residential land use scenario accounts for adult and children residents as receptors. The residential RBCA standards for direct and indirect soil contact in the Tier 1 look-up table (Table 6.1.2.a) are based on the risk-based COC concentrations for a 30-year, time-weighted average residential exposure for adults and children[1].

The non-residential land use scenario accounts only for adult receptors in a commercial-industrial worker setting. The non-residential RBCA standards for soil exposures in the Tier 1 look-up table are based on a 25 year exposure scenario. The equations used to derived the Tier 1 soil standards, otherwise known as the Arizona Soil Remediation Levels (SRLs), are those that were used in the determination of Preliminary Remediation Goals (PRGs) by EPA (EPA, 1991b; EPA1999b). These equations are described in Appendix P of this guidance document.

The Tier 1 RBCA standards for groundwater are the same for both the residential and non-residential exposure scenario, and are based upon drinking water standards. Thus, the primary drinking water standards published by the EPA Office of Drinking Water for Maximum Contaminant Levels (MCLs) in 1986 are the Tier 1 RBCA standards for exposures to contaminated groundwater. For those chemicals which do not have MCLs,

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[1] Tier 1 standards for soil direct and indirect contact are calculated for a time-weighted childhood through adult 30 year period for COCs which are carcinogenic. For those COCs which are non-carcinogenic, the standard is based on a 6 year childhood exposure. The Tier 1 standard is the lower of the two values when a COC has both carcinogenic and non-carcinogenic health affects.

the recommended Tier 1 standard is calculated using the same risk-based methodology as described in Appendix P of this guidance document.

6.2.2 Tier 1 Representative Concentrations

Unless the Tier 1 site characterization has special reasons why it should be extensive with random or systematic sampling (*cf.*, Keith, 1991) of multiple environmental media, sampling is conducted to find the maximum occurrence of environmental contamination with as small a number of samples as possible. The basis for using this approach is a thorough description of the site history, where on the site various chemical materials were used, what those materials were, and what the likely release amount and date were. The history presents the basis for a logic leading to the areas and media to be sampled. This approach has been called *authoritative*, *biased*, *judgmental*, or *purposive*, where each of these titles refer to the same approach (EPA, 1992a). The result of authoritative sampling is a data set where the maximum concentrations of the COCs are "representative" of the maximum concentrations for the site. There is no information about the distribution of COC concentrations over the expanse of the site, so there is no basis to calculate an average concentration and an upper confidence limit estimate. Therefore, **maximum concentrations must be used for Tier 1 evaluation**. This is a conservative measure in addition to the conservative risk-based concentrations to be used in the evaluation that were already determined using upper-bound exposure parameters. These multiple conservatisms help ensure that uncertainties in the evaluation favor false positive (Type I) errors over false negative (Type II) errors for public health protection in decision making.

Maximum concentrations for COCs in environmental media are linked to the point of compliance for each medium. For **soil**, the site-specific location of the maximum COC concentrations in surface (0 -15 ft. bgs) and subsurface soil (>15 ft. bgs) is tied to site history and materials use. This interval for surface soils has been selected in order to care for non-restricted future residential uses of a property. Within reason, a property owner may elect to construct a pool, play center, etc. In doing so, the depth of 15 feet typically can not be exceeded by use of common backhoe construction equipment. Soils at the reach of the backhoe may be brought to the surface where it will remain available for direct contact. For **groundwater**, either the location of the source of the impact or the location of maximum concentrations of the COCs is determined from site characterization. For **surface water**, the location of the point source discharge and/or locations of groundwater/surface water interface must be characterized for maximum

COC concentrations. [Natural wetlands are almost always an interface between surface water and groundwater.]

6.2.3 Comparison of Tier 1 Standards to Representative Site Concentrations

The maximum concentration measured at the site for any COC is compared to the Tier 1 corrective action standard listed in the lookup table, Table 6.1.2.a. If the site concentration for all COCs are less than the Tier 1 value, no further corrective actions are warranted. However, if one or more COCs exceed the Tier 1 value, only these COCs should be evaluated for remediation or evaluation at the Tier 2 level. In determining whether remediation or further risk-based Tier 2 evaluation should be conducted, preliminary screening level calculations should be done and assessed relative to the difference in cost in meeting either the Tier 1 or Tier 2 RBCA standard. In some cases, a screening level Tier 2 may yield a standard which is still exceeded by existing site concentrations. Remedial action would still be required, but the cost of using the same remedial technology would not change in achieving either the Tier 1 or Tier 2 standard. However, an institutional control may result in a more protective level of human health and may be cheaper than active remediation. These factors should be weighted prior to conducting remedial actions or collecting additional site-specific data in support of the Tier 2 calculations.

6.3 Tier 2 Evaluation

The Tier 1 evaluation essentially provides a conservative screening level for site evaluation of contamination. Because the assumptions of the Tier 1 evaluation are generically applied to all sites, it does not necessarily represent actual site conditions. Conducting the Tier 2 evaluation beyond the Tier 1 screening offers the prospect of an assessment which reflects the more realistic assessment based on site-specific data.

The Tier 2 evaluation allows for incorporation of alternate land use, *i.e.* land use, with applicable receptors, *i.e.* adults and no children, where justified. It also allows for refinement of the exposure point concentration of COCs, the point of compliance at which exposure is assumed to occur within the property boundaries, the use of institutional or engineering controls to eliminate exposure pathways or reduce exposures, and site-specifically measured parameters used in the Tier 2 models or equations.   Justification for these variations from the Tier 1 methodology/assumptions must be presented in the Tier 2 evaluation which may be a stand alone document, or submitted in conjunction with the SCR or CAP.

In addition, site-specific documentation of the parameters of the exposure equation may justify use of other than the default values used in Tier 1, resulting in as much as an order of magnitude change in the risk evaluation. For instance, proper documentation of Exposure Frequency or Duration, Fraction Ingested, Body Weight, and Averaging Time may support a receptor survey with site-specific receptor exposure parameters. In that case, justification must be provided in the CAP and in the corrective action report on the upper-bound and average values of the modified exposure parameter(s). For instance, it is not sufficient to report that everyone who works on the site weighs 220 pounds, and, therefore, the body weight should be 100 kg instead of the default value of 70 kg. Inspection of EPA's Supplemental Guidance on Standard Default Exposure Factors (EPA, 1991a) and Exposure Factors Handbook (EPA, 1997a) indicates that 70 kg body weight is an average value (as is Averaging Time), while Exposure Frequency and Duration are upper-bound values, usually 90th percentile. It may be appropriate to cite 100 kg as an upper bound value for that site-specific case, but a parallel evaluation using 70 kg would also have to be included in the report.

In summary, it is expected that evaluation of a residential land use exposure scenario will be accompanied by evaluation for adults and children, while evaluation for commercial-industrial land use (or any justified alternate land use) will include evaluation for the appropriate receptors associated with the land use now and during the next 30 years.

6.3.1 Tier 2 Representative Concentrations

For Tier 2, the consideration of points of compliance (locations) are the same as in Tier 1, *i.e.*, levels of COCs must be less than or equal to the appropriate corrective action standard throughout all locations within the property boundaries. However, the exposure point concentration is quite different. In Tier 1, it is assumed that the maximum concentration is the representative concentration for receptor exposure. In Tier 2, site characterization data can be evaluated to more realistically determine site-specific COC concentrations to define the exposure point concentrations .

There is a way to use authoritative data from Tier 1 site characterization in calculating average and upper-bound COC concentrations. That is to conduct additional site characterization to delineate an AOC or stratum. The COC data inside the AOC, may be used to calculate a mean (average) and upper confidence limit concentration for risk-based evaluation, even though the sampling data were not obtained using a random or systematic sampling rationale (EPA, 1992a, Section 3.2.8, page 55).

It was mentioned previously that the boundaries of an AOC are defined by risk-based concentrations of the COCs. Depending on the land use, those risk-based concentrations may have been determined for a residential or a commercial-industrial land use. Presumably, soil samples taken outside the boundary have COC concentrations less than residential (10^{-6} ILCR/1.0 HQ) or commercial-industrial (10^{-5} ILCR/1.0 HQ), *de minimis* risk/hazard, and are of no further concern. The samples inside the boundary have COC concentrations that are biased toward high concentrations because they were originally obtained in the pursuit of the maximum concentrations of the COCs. Therefore, averaging the sample concentrations inside the boundary should yield an "average" that is biased higher than the true mean of the real distribution of COC concentrations that would be representative of the site, if it were known. A biased-high average will yield a 95% UCL that is also biased-high (and may even exceed the respective maximum COC concentration, in which case, the maximum value is used). This process allows the opportunity to determine more representative COC concentrations with the prospect of a more realistic, representative assessment for risk-based decision making.

To calculate the 95% UCL on the mean of the data set, various methods may be used and are dependent upon the data distribution conforming to the Gaussian distribution, or normal distribution. Statistical methods applied for this type of data set are parametric. Non-normal distributions rely preferably on non-parametric methods. A discussion on environmental statistical methodology is beyond the scope of this guidance document. However, statistical methods are provided in the Tier 2 RBCA software and are limited to determination of the 95% UCL on the mean. In cases when the 95% UCL is greater than the maximum concentration, the maximum concentration must be used as the Tier 2 representative concentration.

6.3.2 Screening Process for Proceeding with Tier 2 Evaluation

Once you have completed site characterization and have evaluated site concentrations relative to the Tier 1 corrective action standards, you must decide if Tier 2 evaluation and remediation is more appropriate for your site than cleanup to Tier 1 levels. The decision logic for whether to conduct a Tier 2 evaluation is based on a comparison of the difference in the cost of remediation between Tier 1 and Tier 2 standards versus the cost of further study in Tier 2. The ease of this decision is facilitated with the Tier 2 RBCA software in which value estimates of site-specific parameters are substituted for the defaults values in the Tier 1 equations. The outcome of this screening level Tier 2 provides the basis for evaluating the costs associated

with additional data collection, and the costs associated with achieving the Tier 2 site-specific corrective action level.

Questions that should be considered in evaluating whether to proceed with Tier 2 are:

C   Is the basis, or are the assumptions used to derive the current tier's goals appropriate for conditions at this site?

For instance, the potential receptors associated with a site might only be in the vicinity of the exposure location for a fraction of the time of the default parameter used in developing the numerical Tier 1 corrective action standard or the Tier 2 site-specific corrective action standard. Further investigation of site-specific human actions may support parameter modifications that could account for substantial reduction in the stringency of the site-specific corrective action standard in Tier 2.

C   Will site-specific corrective action standards developed under Tier 2 be significantly different than Tier 1 numerical corrective action standards?

The Tier 2 comparison of the representative COC concentrations to site-specific corrective action standards provides an excellent comparison for the more detailed analysis results needed to demonstrate acceptable site-specific conditions while meeting health protective standards. Is the representative COC concentration a small percentage different than the Tier 2 site-specific corrective action standard? Or is it more than an order of magnitude different? Can Tier 2 evaluation, perhaps coupled with limited remedial action, affect enough of a change in each representative site COC concentration to meet each respective risk-based criterion?

C   Will site-specific corrective action standards developed under Tier 2 significantly modify the remedial action activities?

For instance, if the benzene numerical corrective action standard is driving the need for cleanup, will Tier 2 evaluation provide a revised, less restrictive benzene site-specific corrective action standard that still meets the same level of health protection and shifts the driver for cleanup to a non-cancer COC, such as toluene, where the remedial action will be significantly reduced in approach or extent of action?

C   Will the cost of remedial action to Tier 1 numerical corrective action standards likely be greater than further tier evaluation and subsequent remedial action?

The comparison of costs for various options is not always easy to construct accurately. Often, USTs present a manageable case where Tier 1 results are convincing enough to proceed with remediation just to be done with the problem at hand. However, it should be remembered that Tier 1 often involves estimates based on modeling that have to be confirmed by environmental monitoring over time at additional cost.

All these factors should be considered when deciding on whether to conduct Tier 2 evaluation.

6.3.3   Site-Specific Data and Data Requirements

Tier 2 evaluation can take several approaches to make the assessment more site-specific.

The site characterization data itself can be extended to further characterize the expanse and extent of contamination. The receptor survey can be refined for the human activity and physiology parameters that are applicable. And the site-specific geotechnical data can be refined for site-specific input to the numerical fate and transport models used to estimate indirect exposure pathways.

Tier 2 modification of the Tier 1 relationships can be conducted by substituting site-specific parameters for the default parameters used in calculating numerical corrective action standards [EPA Region IX PRGs (EPA, 1999b) are used as numerical corrective action standards in the Tier 1 evaluation]. The substitution process consists of multiplying/dividing the new & default parameters to transform the RBSL to a SSTL for site-specific characteristics. An example illustrates how this is done.

Considering the equation for the risk-based site-specific standard (risk-based concentration, RBC) for incidental ingestion exposure to a carcinogenic COC in soil,

$$RBC_{soil} = \frac{AT \times BW \times R}{SF \times EF \times ED \times IR \times CF \times FI}$$

(Equation 6.3.2.1)

exposure frequency can be refined from 250 days/year to 200 days/year by multiplying by the Tier 1 EF (250 days/year) to "divide out" the old EF to 1, then inserting the new EF by dividing by 200 days/year, the new EF for Tier 2. Similarly, the fraction ingested, FI is a factor that incorporates other aspects of the exposure scenario such as significant difference in the area of bare soil for exposure compared to the size of the entire site. Refinement of the fraction ingested is conducted by multiplying the default FI (1.0) to "divide out" the old FI to 1, then inserting the new FI by dividing by the new FI, 50% in this example.

$$\text{If Tier 1 RBSL = 100 mg/kg for surficial soil exposures,}$$

$$SSTL = (RBSL) \left(\frac{EF_{Tier1}}{EF_{Tier2}} \right) \left(\frac{FI_{Tier1}}{FI_{Tier2}} \right)$$

$$SSTL = (100 \text{ mg/kg}) \left(\frac{250 \text{ days/year}}{200 \text{ days/year}} \right) \left(\frac{100\%}{50\%} \right)$$

$$SSTL = 250 \text{ mg/kg}$$

In the example, a numerical corrective action standard of 100 mg/kg can become a site-specific corrective action standard of 250 mg/kg with justified modification of the exposure parameters. The difference in the cost to remediate to these two corrective action standards or the savings by remediating to only the higher, less stringent corrective action standard can be significant.

This same kind of refinement can be conducted for any of the relationships in the CSM, *i.e.*, volatilization factor, leaching factor, or dilution attenuation factors for unsaturated or saturated soil.

6.3.3.1   Site Characterization Data

Refinement of site characterization data often involves additional sampling to delineate the three-dimensional extent of COC contamination for determination of an area of concern (AOC). This is discussed in more detail in Section 6.3.8 on representative concentrations. For Tier 2, refinement of the AOC is conducted by better defining those locations at which concentrations **exceed** the Tier 1 corrective action standard. Using this additional data, the 95% UCL on the mean may be calculated and compared

with the Tier 2 site-specific corrective action standard which relies on additional site data other than contaminant concentrations. This results in reducing the volumetric definition of environmental media exceeding the remediation standard, by virtue of the Tier 2 standard being a concentration higher than that of the Tier 1 standard.

Refinement of geotechnical parameters can be achieved with additional sampling, but care must be taken to present proper documentation in the risk assessment report that the results are consistent with soil lithology across the area including the site and the boring logs developed from the site investigation. Geotechnical parameters that are sensitive parameters in fate and transport models, and most likely to offer benefit by additional characterization, are enumerated in Section 6.3.5.1.

6.3.3.2   Exposure Factors

Exposure factors describe the physiological and activity characteristics of the receptor. These include factors such as the body weight, body surface area, air inhalation rates, water ingestion rate, and more. The exposure factors are typically estimated based on literature values, and site-specific measurements are not conducted. A list of default exposure factors to be used for Tier 1 and Tier 2 evaluations are presented in the Preamble Appendix B to A.A.C. Title 18, Chapter 7, Article 2. The specific default exposure values represent the reasonable maximum exposure (RME) values defined as the highest exposure that is reasonably expected to occur at a site (EPA, 1989a). Unless there is substantiation to use alternate values, it is expected that the default exposure parameters will be used for risk assessment and development of site-specific corrective action standards.

6.3.3.3   Fate and Transport Parameters

Fate and transport parameters are necessary to develop site-specific corrective action standards for the indirect pathways of exposure, *i.e.*, volatilization from soil or groundwater; leaching from soil. These factors characterize the soil, groundwater, windspeed, and infiltration rate at a site. For Tier 1 numerical corrective action standards, the ADEQ has selected generic, conservative default values that are listed in the September 1996 ADEQ Soil Screening Levels Protective of Leaching to Groundwater. For a Tier 2 evaluation, a combination of site-specific and generic values for these parameters may be used. However, the value of each parameter used must be justified based on site-specfic conditions. For a Tier 3 evaluation (see Section 6.4), the specific fate and transport parameters required to compute

the target levels will depend on the choice of models. Discussion of those parameters for Tier 2 (and by implication for Tier 3) may be found in Sections 6.3.5.1 through 6.3.5.6.

6.3.4 Revising the CSM

The CSM is confirmed or revised based on the site characterization for the Tier 2 evaluation. If the site characterization from the Tier 1 study is not advanced by a second field mobilization, then all the other new information since the Tier 1 investigation should be incorporated to update the CSM. More specifically, the following items incorporated in the CSM must be confirmed or revised in finalizing the CSM.

C   The inventory of sources, pathways, and receptors [Has more been learned about the nature and magnitude of the source(s)?];

C   The environmental media and release/transport mechanisms [Can media, like surface water, be ruled out based on the site characterization?];

C   Land use, both current and future (nominally 30 years) [Will it remain the same? Is there potential for a higher and better land use?];

C   Receptor survey [Are there differences between the standard receptors for an exposure scenario and those found on/around the site now and likely in the future?];

C   Site setting [Are there natural or man-made features (institutional controls) that provide current exposure protection, but may be removed in the future?];

C   Off-site receptors and property development [Are there developments of nearby properties that might occur (or be ruled out), affecting the constituency of off-site receptors?];

C   Point(s) of Exposure (POEs) [Do the locations and receptors at those locations remain the same?]; and

C   COC list [Has the list of COCs remained the same? If there is a change, does the change affect the conceptual understanding of fate & transport processes for the site? Is the list of COCs different for different environmental media, exposure pathways, and receptors?].

With regard to revisions to the CSM for future land use changes, those which account for a change from residential to commercial/industrial represent no further concern or evaluation, as residential standards are more stringent than those for non-residential uses. However, land use changes from commercial/industrial to residential represent a potential for site characterization and corrective actions to be conducted in accordance with the more stringent levels of residential use. As it is not cost-effective to delineate and remediate a commercial/industrial property to residential Tier 1 standards relative to the cost of implementing a non-residential use restriction DEUR, this change should not be evaluated for the future in the CSM unless cost-savings is eliminated from the tiered evaluation. This change should be accounted for if current land uses change prior to completion of corrective actions and site closure.

The confirmation or revision of the CSM must reflect all that is known about the site and surroundings. The revised CSM then becomes the basis for the risk-based evaluation conducted in Tier 2. While some exposure pathways can be ruled out or confirmed based on the site history and characterization, the risk-based evaluation may indicate that some potentially-complete pathways have insignificant/*de minimis* risk/hazard. Pathways with significant risk/hazard ($>10^{-6}$ ELCR and/or 1 HI) can be addressed with a focused remedy (engineering and/or institutional controls) and/or further analysis in Tier 3.

6.3.5 Modeling Applications for Determining the Tier 2 Corrective Action Standards

The EPA Region IX PRGs constitute Tier 1 Corrective Action Standards. These standards are comparable to risk-based screening levels (RBSLs) in the nomenclature of the ASTM RBCA standard (ASTM, 1995), assuming, of course, that they are based on the same equations and parameters. Any modification of numerical corrective action standards based on better site-specific knowledge results in Tier 2 site-specific corrective action standards. The calculation of site-specific corrective action standards involves the use of equations or models applicable to the respective pathways and fate & transport processes.

A risk-based decision making process requires the specification of a target risk level for both carcinogenic and non-carcinogenic adverse health effects. The target risk levels are used to estimate the target exposure point concentrations. ADEQ will accept risk-based concentrations for Class A

carcinogens (known human carcinogens) back-calculated using 10^{-6} ELCR as the target risk. For possible/probable human carcinogens (Classes B1, B2, C), risk-based concentrations back-calculated using 10^{-5} ELCR as the target risk are acceptable. Risk-based concentrations using these criteria for the usual UST petroleum hydrocarbons (HC_{10-32}) and BTEX analytes provides, in all but the most unusual circumstances, that the NCP (EPA, 1990) criterion for acceptable exposure of 10^{-4} ELCR is met. Characterization of **carcinogenic** properties of petroleum hydrocarbons (HC_{10-32}) should be based on chemical-specific analyses and evaluation of analytes present in environmental samples for which there is a cancer slope factor, such as individual PAHs detectable using US EPA SW-846 Method 8310 or 8270BN. A general evaluation for petroleum hydrocarbons (HC_{10-32}) should not be conducted using the slope factor for diesel. Corrective action standards for **non-carcinogenic** effects of petroleum hydrocarbons (HC_{10-32}) can be calculated readily for petroleum hydrocarbon (HC_{10-32}) fractions (as in Section 6.1.2) using the toxicity factors of the TPHCWG (Edwards, et al, 1997). There are at least two software packages that can aid in calculation of risk-based concentrations for petroleum hydrocarbon (HC_{10-32}) fractions (GSI, 1999; RISC, 1997).

Two types of models or equations, namely (i) the uptake equations and (ii) the fate and transport models are required to calculate the corrective action standards. For Tier 1 and Tier 2 evaluations, the ADEQ has selected the models and equations presented in the Equations section at the end of Section 6.3. These models have been programmed in the ADEQ Corrective Action Software and correspond to the EPA Region IX PRGs used as numerical corrective action standards for the Tier 1 screening evaluation. For Tier 2 evaluations, the ADEQ requires the use of the Section 6.3 equations and models. For Tier 3, any model presented in the ASTM document titled *RBCA Fate and Transport Models: Compendium and Selection Guidance* (ASTM, 1999) may be used with greater detail (SESOIL with more inputs for documented soil lithology, for instance). Other models may be used for Tier 3 evaluation with prior approval of ADEQ. Additional time and effort will need to be budgeted for biefing of ADEQ staff on Tier 3 models not routinely used in RBCA evaluations for Tiers 1 and 2.

6.3.5.1   Soil Vapor Flux and Dispersion (Indoor and Outdoor): Vapor Inhalation

The fate and transport models used to estimate volatile emissions from soil and groundwater require information about the soils in the vadose zone. The specific parameters required include:

C   Soil bulk density for the vadose zone;
C   Organic carbon content in the vadose zone;
C   Porosity in the vadose zone;
C   Water content in the vadose zone; and
C   Air content in the vadose zone.

It is important to note that the sum of the water content and the air content must equal the porosity. Methods used to measure these parameters are discussed in the ADEQ guidance documents downloadable in the future at links available through the UST Program website, http://www.adeq.state.az.us/environ/waste/ust/.

Several other parameters are required to estimate the target levels for indoor and outdoor inhalation. These include:

C   Air exchange rate in the building that depends on the construction of the building. Default values listed in Appendix P may be used for Tier 1 as well as Tier 2 evaluation. Literature values may be obtained by researching architectural and building design publications, the ASTM Standard Guide (ASTM, 1995), building code specifications;

C   Height of the enclosed space, typically equal to the height of the first floor of the building;

C   Areal fraction of cracks in the foundation of the building; the default for the crack length in this determination is the circumference of the basement or slab on grade in contact with the building where vapors may enter;

C   Outdoor wind speed in the breathing zone;

C   Height of the outdoor breathing space, typically estimated as 200 cm;

C   Length of soil source parallel to the wind direction. This parameter is estimated based on the size of the contaminated soil or groundwater source based on site characterization;

C   Depth to contaminants in soil; and

C   Depth to groundwater.

6.3.5.2   Dermal Direct Contact with Soil

The equation used to calculate the numerical corrective action standard (Tier 1) for direct contact with carcinogenic COCs, including ingestion, inhalation, and dermal exposure routes, in residential soil is

$$RBC_{res\&c\&soil} ' \frac{R \ x \ AT_c}{EF_r \ [(\frac{IFS_{adj} \ x \ SF_o}{CF}) \ \% \ (\frac{SFS_{adj} \ x \ ABS \ x \ SF_o}{CF}) \ \% \ (\frac{InhF_{adj} \ x \ SF_i}{VF_s^a})]}$$

D
efinition of the various parameters is listed in Appendix O. For exposure based only on the dermal contact absorption pathway, this equation reduces to

$$RBC_{res\&dermal\&c\&soil} ' \frac{R \ x \ AT_c}{EF_r \ [(\frac{SFS_{adj} \ x \ ABS \ x \ SF_o}{CF})]}$$

where the term, SFS_{adj}, reflects exposure to adults (a) and children (c), and includes the parameters

$$SFS_{adj} ' \frac{ED_c \ x \ AF \ x \ SA_c}{BW_c} \ \% \ \frac{(ED_r \ \& \ ED_c) \ x \ AF \ x \ SA_a}{BW_a}$$

The default exposure factors and their definitions for all the numerical corrective action standards (Tier 1) are listed in Appendix O and apply here also. The terms describing the intake rate for dermal contact absorption for soil are

SA   =   Skin Surface Area (child, c, or adult, a) Available for Contact (cm^2/event)
AF   =   Soil-to-Skin Area Available for Contact, also called Adherence Factor (cm^2/event)
ABS   =   Absorption Factor (unitless)
EF   =   Exposure Frequency (events/year)

Exposure factors for dermal contact with soil have changed recently (EPA 1999c). Recommended RME defaults for adult workers' skin surface areas (3300 cm^2/day) and soil adherence factors (0.2 mg/cm^2) now differ from the defaults recommended for adult residents (5700 cm^2/day, 0.07 mg/cm^2) as

noted in Exhibit 4-1 of EPA, 1999c. This is due to differences in the range of activities experienced by workers versus residents.

Chemical-specific skin absorption values (EPA, 1999c) should be used when available. Chemical-specific values for the following chemicals: arsenic, cadmium, chlordane, 2,4-D, DDT, lindane, TCDD, PAHs, PCBs, and pentachlorophenols may be found in EPA, 1999c.

"Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) Interim Guidance" (USEPA 1999c) recommends a default dermal absorption factor for semivolatile organic compounds of 10% as a screening method for the majority of SVOCs without dermal absorption factors. Default dermal absorption values for other chemicals (VOCs and inorganics) are not recommended in the new guidance. Therefore, the assumption of 1% for inorganics and 10% for volatiles is no longer included in the EPA Region 9 PRG table. This change has minimal impact on the final risk-based calculations because human exposure to VOCs and inorganics in soils is generally driven by other pathways of exposure.

In Tier 2, site-specific information can be used with substantiation. Justification must be provided to rule out other direct soil exposure routes (ingestion and inhalation) in the CSM. Otherwise those routes must be included, and the site-specific corrective action standard must include those terms for calculation of the standard. These options are available in the downloadable software, and description of the options chosen in using the software must be provided in the risk assessment report.

Calculation of the site-specific corrective action standard for dermal contact absorption of noncarcinogenic COCs in residential soil is based on the risk-based equation, as in Section 6.2,

$$RBC_{res\&n\&soil} = \frac{THQ \times BW_c \times AT_n}{EF_r \times ED_c \left[\left(\frac{1}{RfD_o} \times \frac{IRS_c}{CF}\right) \% \left(\frac{1}{RfD_o} \times \frac{SA_c \times AF \times ABS}{CF}\right) \% \left(\frac{1}{RfD_i} \times \frac{IRA_c}{VF_s^a}\right)\right]}$$

and the reduced equation for only a dermal pathway is

$$RBC_{res\&dermal\&n\&soil} = \frac{THQ \times BW_c \times AT_n}{EF_r \times ED_c \left[\left(\frac{1}{RfD_o} \times \frac{SA_c \times AF \times ABS}{CF}\right)\right]}$$

The equations for commecial-industrial land use are similar, but are based on exposure to only adults (a). For instance, the equation for the commercial-industrial dermal carcinogenic soil site-specific corrective action standard is

$$RBC_{occ\&dermal\&c\&soil} \; ' \; \cfrac{R \; x \; BW_a \; x \; AT_c}{EF_o \; x \; ED_o \; [(\cfrac{SA_a \; x \; AF \; x \; ABS \; x \; SF_o}{CF})]}$$

The equation for the commercial-industrial dermal non-carcinogenic soil site-specific corrective action standard is

$$RBC_{occ\&dermal\&n\&soil} \; ' \; \cfrac{THQ \; x \; BW_a \; x \; AT_n}{EF_o \; x \; ED_o[(\cfrac{1}{RfD_o} \; x \; \cfrac{SA_a \; x \; AF \; x \; ABS}{CF})]}$$

Calculation of the Tier 2 site-specific corrective action standard for either carcinogenic or non-carcinogenic COCs involves using either default factors or alternate values substantiated with site-specific information. All of this guidance can be implemented through the downloadable software from the d e p a r t m e n t w e b p a g e (U R L : *http://www.adeq.state.az.us/environ/waste/ust/cap.html*).

6.3.5.3   Dermal Direct Contact with Groundwater and Surface Water

Dermal contact absorption of COCs in groundwater or surface water is an important potential exposure pathway in Arizona because of the availability of surface water and lagoons of pumped groundwater at many locations throughout the state. Exposure can also occur during household use (e.g., bathing, showering) or while swimming or wading. Since there are no promulgated ambient water quality criteria concentrations for dermal exposure to water, a risk-based corrective action standard should be calculated. The exposure is evaluated beginning with the intake equation from EPA, 1989a (Exhibit 6-13)

$$\textit{Intake}\,(\textit{mg/kg\&day}) \; ' \; \cfrac{(\textbf{\textit{C}}_W \; x \; \textbf{\textit{SA}} \; x \; \textbf{\textit{K}}_p \; x \; \textbf{\textit{ET}} \; x \; \textbf{\textit{EF}} \; x \; \textbf{\textit{ED}} \; x \; \textbf{\textit{VCF}})}{(\textbf{\textit{BW}} \; x \; \textbf{\textit{AT}})}$$

where the parameters have the definitions presented in Section 6.3.2 with addition of the following:

C_w = COC concentration (maximum or representative) in groundwater or surface water (mg/L)

SA = Skin Surface Area Available for Contact (cm^2/event)

K_p = Chemical-specific Dermal Permeability Constant (cm/hr, also called PC).

ET = Exposure Time (hours/day).

VCF = Volumetric Conversion Factor for water (1 liter/1000 cm^3)

The Tier 1 numerical corrective action standards for groundwater include component contributions for ingestion and inhalation exposure, but not dermal contact absorption exposure. The above equation can be applied to develop the equations for calculating Tier 2 site-specific corrective action standards for dermal contact absorption exposure.

In a residential setting, there can be exposure to both adults and children. Therefore, the intake for a 30-year (90th percentile, Reasonable Maximum Exposure) residential tenure is made up of contributions for childhood exposure (6 years) and adult exposure (24 years). The equation for the corrective action standard for dermal exposure to water in a residential setting, corrected for concentration units of μg/L, is

$$RBC(\mu g/L)_{res\&dermal\&c\&water} \cdot \frac{R \times AT_c \times 1{,}000\ \mu g/mg}{SF_o \times K_p \times VCF} \times \frac{(BW_a \% BW_c)}{(SA_a \times ET_a \times EF_a \times ED_a) \% (SA_c \times ET_c \times EF_c\ ED_c)}$$

where the parameters have the following descriptions:

$RBC(\mu g/L)_{res\text{-}dermal\text{-}c\text{-}water}$ = site-specific Corrective Action Standard, residential exposure scenario, dermal exposure route, cancer end point, water medium

R = Target Risk, 10^{-6} ELCR for benzene (Class A carcinogen)

AT_c = Averaging Time for carcinogenic exposure, 70 years whether adult (a) or child (c)

1,000 μg/mg = correction factor to convert mg/L to μg/L

SF_o	=	Chemical-specific cancer slope factor for oral exposure route, used as a surrogate for the dermal exposure route
K_p	=	Chemical-specific dermal permeability coefficient, also sometimes called PC, in cm/hr
VCF	=	Volumetric conversion factor for water (1 L/1000 cm^3)
BW	=	Body weight for adult (a, 70 kg) or child (c, 15 kg)
SA	=	Skin surface area available for contact (cm^2)
ET	=	Exposure time (hr/day) based on local activity patterns; 2.6 hr/day national average for swimming (EPA, 1988b; EPA, 1989c)
EF	=	Exposure frequency, based on local climate and activity patterns; 7 days/yr national average for swimming (EPA, 1988b; EPA, 1989c)
ED	=	Exposure duration for children (c, 6 years) and adults (a, 24 years)

For non-carcinogens, the equation for the site-specific corrective action standard is

$$RBC(\mu g/L)_{res\&dermal\&n\&water} \cdot \frac{THQ \ x \ AT_c \ x \ 1{,}000 \ \mu g/mg}{[\ \frac{1}{RfD_o} \ x \ K_p \ x \ VCF\ ]} \ x \ \frac{(BW_a \ \% \ BW_c)}{[(SA_a \ x \ ET_a \ x \ EF_a \ x \ ED_a) \ \% \ (SA_c \ x \ ET_c \ x \ EF_c \ ED_c)]}$$

where parameters different than the cancer-based equation are

THQ	=	Target hazard quotient, usually 1.0
RfD_o	=	Reference dose for oral exposure route as surrogate for dermal exposure route.

Calculation of a site-specific corrective action standard is based on a residential exposure scenario because future land use may be residential regardless of the current land use. Further, groundwater and surface water may travel some distance from the point of contamination to a location where exposure in a residential setting can occur (EPA, 1990, page 8717, column 2, paragraph 3; EPA, 1991b, page 13, column 2, paragraph 4). Protection of the groundwater to residential standards is consistent with the mandate of the State of Arizona to protect the waters of the state from degradation (A.A.C. R18-11-405 and R18-11-108).

However, it is likely that risks calculated for occupational exposure will be higher than those for residential exposure because of longer exposure time, frequency, and duration of occupational exposures. Therefore, where dermal exposure is likely in an occupational setting, a corrective action should be developed as part of the risk assessment report.

If a situation does arise where the site-specific corrective action standard may be set based on exposure in a commercial-industrial setting, such as a worker in a fishery or reservoir, the equation for the residential setting reduces to terms for adult exposure only, as follows

$$RBC(\mu g/L)_{comm\&dermal\&c\&water} \cdot \frac{R \; x \; AT_c \; x \; BW_a \; x \; 1,000 \; \mu g/mg}{SF_o \; x \; K_p \; x \; CF \; x \; SA_a \; x \; ET_a \; x \; EF_a \; x \; ED_a}$$

where terms for a commercial-industrial exposure scenario are

R = Target risk, 10^{-5} for industrial sites in Arizona, consistent with the development and implementation of SRLs in A.R.S. § 49-151, 49-152, 49-282.06

SA = Skin surface area available for contact (cm^2)

ET = Exposure time for occupational exposure, job-specific (hr/day)

EF = Exposure frequency (days/year, 250 days/yr default)

ED = Exposure duration (years, 25 year default for occupational tenure)

For non-carcinogens the equation for the site-specific corrective action standard is

$$RBC \; (\mu g/L)_{comm\&dermal\&n\&water} \cdot \frac{THQ \; x \; AT_c \; x \; BW_a \; x \; 1,000 \; \mu g/mg}{[\; \frac{1}{RfD_o} \; x \; K_p \; x \; VCF \; x \; SA_a \; x \; ET_a \; x \; EF_a \; x \; ED_a \;]}$$

which can be rearranged to

$$RBC \; (\mu g/L)_{comm\&dermal\&n\&water} \cdot \frac{RfD_o \; x \; THQ \; x \; AT_c \; x \; BW_a \; x \; 1,000 \; \mu g/mg}{[\; K_p \; x \; VCF \; x \; SA_a \; x \; ET_a \; x \; EF_a \; x \; ED_a \;]}$$

These equations can be implemented, as needed, through the ADEQ software, soon downloadable at http://www.adeq.state.az.us/environ/waste/ust/cap.html.

6.3.5.4   Ingestion of Soil

Calculation of risk-based PRGs for direct ingestion of soil is based on methods presented in *RAGS HHEM, Part B* (USEPA 1991a) and *Soil Screening Guidance* (USEPA 1996a,b). Briefly, these methods back-calculate a soil concentration level from a target risk (for carcinogens) or hazard quotient (for noncarcinogens).

A number of studies have shown that inadvertent ingestion of soil is common among children 6 years old and younger (Calabrese et al. 1989, Davis et al. 1990, Van Wijnen et al. 1990). To take into account the higher soil intake rate for children, two different approaches are used to estimate numeric corrective action standards, depending on whether the adverse health effect is cancer or a health effect other than cancer.

For carcinogens, the method for calculating PRGs uses an age-adjusted soil ingestion factor that takes into account the difference in daily soil ingestion rates, body weights, and exposure duration for children from 1 to 6 years old and others from 7 to 31 years old. This health-protective approach is chosen to take into account the higher daily rates of soil ingestion in children as well as the longer duration of exposure that is anticipated for a long-term resident. For more on this method, see *USEPA RAGs Part B* (1991a).

For noncarcinogenic concerns, the more protective method of calculating a soil corrective action standard is to evaluate childhood exposures separately from adult exposures. In other words, an age-adjustment factor is not applied as was done for carcinogens. This approach is considered conservative because it combines the higher 6-year exposure for children with chronic toxicity criteria. In their analysis of the method, the Science Advisory Board (SAB) indicated that, for most chemicals, the approach may be overly protective. However, they noted that there are specific instances when the chronic RfD may be based on endpoints of toxicity that are specific to children (*e.g.*, fluoride and nitrates) or when the dose-response is steep (*i.e.*, the dosage difference between the no-observed-adverse-effects level [NOAEL] and an adverse effects level is small). Thus, for the purposes of screening, This is the approach used for calculating soil corrective action standards for non-carcinogenic health hazard.

6.3.5.5 Ingestion of Fugitive Dusts

Fugitive dust is considered to be particulate 10Fm in diameter or less that can become entrained in the air by wind erosion of the upper six-inch interval of surface soil (EPA, 1985). Fugitive dust is included in the Tier 1 risk-based COC concentration (RBC) as a Particulate Emission Factor (PEF) for non-volatile COCs for residential land use (EPA, 1999b, equation 4-1). [Volatile COCs are evaluated in equation 4-1 by using a volatilization factor, VF_s, in place of the PEF.] Of the COCs inspired on fugitive dust particles, 25% are exhaled and 75% are retained in the lungs. Readily soluble compounds are taken into the body rapidly, while other compounds may be eliminated from the lungs and swallowed in the first 24 hours (12.5%) or retained in the lungs (12.5%) with a half-life of 120 days while being absorbed into body fluids (EPA, 1985). As a conservative estimate for risk assessment, it is assumed that all the COCs adsorbed onto fugitive dust are taken into the body. This is consistent, by comparison, with toxicity standards that are based on administered dose and not absorbed dose, for which data are much less plentiful.

6.3.5.6 Inhalation of Vapors from Groundwater and Surface Water

Calculation of corrective action standards for ingestion and inhalation of contaminants in domestic water is based on the methodology presented in (USEPA 1991a). Ingestion of drinking water is an appropriate pathway for all chemicals. For the purposes of this guidance, however, inhalation of volatile chemicals from water is considered routinely only for chemicals with a Henry's Law constant of 1×10^{-5} atm-m^3/mole or greater <u>and</u> with a molecular weight of less than 200 g/mole. BTEX components meet these criteria.

For volatile chemicals, an upperbound volatilization constant (VF_w) is used that is based on all uses of household water (e.g showering, laundering, and dish washing). Certain assumptions were made. For example, it is assumed that the volume of water used in a residence for a family of four is 720 L/day, the volume of the dwelling is 150,000 L and the air exchange rate is 0.25 air changes/hour (Andelman in EPA, 1991a). Furthermore, it is assumed that the average transfer efficiency weighted by water use is 50 percent (*i.e.*, half of the concentration of each chemical in water will be transferred into air by all water uses). Note: the range of transfer efficiencies extends from 30% for toilets to 90% for dishwashers.

6.3.6 Utilization of Non-Site-Specific Assumptions

Conservative default values should be used for the calculation of site-specific standards unless site-specific justification can be documented. Site-specific parameters that require specific site usage, access restriction, or specific personal activity limitations will require institutional controls as part of the site-specific remedy, and, in general, should not be part of the calculation of the site-specific corrective action standard.

6.3.7 Elimination of Select COCs

COCs that do not make a significant contribution to total (cumulative) cancer risk or health hazard may be eliminated from further evaluation. In Tier 1, COC soil concentrations are compared individually to risk-based concentrations, *i.e.*, SRLs, GPLs and numerical corrective action standards. Carcinogenic COCs with soil concentrations that meet SRLs, numeric corrective action standards, **and** minimum GPLs, *i.e.*, present less than 10^{-6} ELCR via those pathways, may be eliminated from further consideration **for those pathways**. If carcinogenic COCs in soil also are found in other environmental media, *e.g.*, surface water, so that cumulative risk is important, as in the Tier 2 (and Tier 3) evaluation, they should be carried forward.

Non-carcinogenic COCs with soil concentrations that are less than 0.1 of the chemical-specific SRL and GPL, and do not contribute to pathways in other media, *e.g.*, surface water, may be eliminated from further consideration in soil.

In the Tier 2 and Tier 3 evaluations, cumulative risk and hazard must be determined in addition to the individual comparison of concentrations with the site-specific standards. Accordingly, COCs must not be eliminated unless their contribution to cumulative risk is shown to be insignificant.

In Tiers 1, 2, and 3, comparison of site-specific concentrations may be made to numeric standards that are promulgated and are not risk-based. Standards such as ambient water quality criteria are examples. Compliance with these standards is sufficient, and evaluation need not be extended to additional tiers of evaluation.

6.3.8 Calculating Representative Concentrations for COCs

The economical and efficient way to characterize a UST release site incorporates site history and practical qualitative information about the physical setting with environmental sampling focused on finding

contamination if it is present. The sampling approach is called *authoritative*, *biased*, *judgemental*, or *purposive*. All these terms refer to the same rationale and result in a finding of the maximum likely concentration of each COC. The vertical and horizontal extent of contamination is usually not obtained from this approach because of the relatively small number of samples collected. To remain conservative for the protection of the public health, evaluation must be based on the maximum concentration found. Once this approach is used for an initial, Tier 1 analysis, it is possible to extend the data set and determine statistical representation of the data for a more representative evaluation.

Tier 2 analysis may be conducted with the maximum concentrations used in Tier 1 or more representative statistics may be determined, sometimes with remobilization and additional field sampling for Tier 2. According to EPA, 1992a (page 55, Section 3.2.8) *"Judgmental samples can be incorporated into a statistical design if the samples designate the area of suspected contamination as an exposure area or stratum. The judgmental samples are then selected randomly or within a grid in the area of known contamination."*
The designation of a three-dimensional stratum for the release makes intuitive sense because it allows a boundary to be drawn on a site map indicating the line of acceptable concentrations of the COCs, which may be chosen as "Not-Detected", minimum GPLs, SRLs, or 10^{-6} ELCR. For whatever criterion is chosen to establish the boundary, the rationale for the choice must be presented in the risk assessment; the stratum should be shown on the site map; and the environmental medium involved, *e.g.* soil, must be consistent with the CSM.

Within a given stratum, the number of samples may be too low for high statistical confidence (about 30 samples required). In such case, statistics may still be used for Tier 2 analysis considering the following rationale. A release to environmental media is not uniform. Concentrations of COCs in soil, for instance, more often than not approximate a log-normal distribution than a normal distribution. The designation of a stratum bounds that release so that the COC concentrations within it are generally above the designated criterion for the AOC boundary. Therefore, an average of the COC concentrations in a stratum should exceed the "true mean" of the expanse of the release that would dissipate to zero concentration with distance. Overestimation of the mean is consistent with conservative evaluation to protect against false negative conclusions, yet provide COC concentrations for evaluation that are lower than the maximum concentration obtained from the judgmental sampling approach. Once a mean concentration is

determined for each COC, the 95% upper confidence limit can be determined using the equation

$$95\%UCL = \overline{X} + t_{(F,n-1)}\left(\frac{s}{\sqrt{n}}\right)$$

where $\overline{X}$ is the mean of the data, s is the standard deviation of the sample (n-1 basis) set, and $t_{(F,n-1)}$ is the critical value. The critical value, t is based on a confidence interval, F, equal, by convention, to 0.95, further equal to 1-a, where a = 0.05, the chance that the mean actually exceeds the 95% UCL (a false negative result, *i.e.* site contamination is greater than the mean but is not assessed as such). The 95% UCL then indicates the concentration for which there is a 95% confidence that the true mean concentration of the COC for the whole stratum is lower.

Typical values of the critical value are listed in the following table.

$t_{(F, n-1)}$ Values for 95th Percentile of Student's t-Distribution, (F = 1-a; n = degrees of freedom)	
n \ F	0.95
3	2.353
4	2.132
6	1.943
12	1.782
18	1.734
24	1.711
30	1.697
4	1.645
Source: CRC Handbook of Tables for Probability and Statistics, 1966, W.H. Beyer, ed., Chemical Rubber Company, Cleveland, OH, printed in EPA, 1989b.	

The 95% UCL and the mean, $\bar{X}$, should be used in the Tier 2 evaluation and reported in the risk assessment. When both are used, it provides a useful perspective over using only the maximum concentration, as in Tier 1.

6.3.9 Comparison of Tier 2 Corrective Action Standard with Site Contamination

A suggested stepwise approach for PRG-screening of sites with multiple pollutants is as follows:

• Perform an extensive records search and compile existing data.
• Identify site contaminants in the look-up table of numeric corrective action standards.
• Record the numeric corrective action standard concentrations for various media and note whether the standard is based on cancer risk (indicated by "ca") or noncancer hazard (indicated by "nc").
• Segregate cancer-based standards from non-cancer standards and exclude (but don't eliminate) non-risk based standards ("sat" or "max").
• For cancer risk estimates, take the site-specific concentration (maximum or 95 UCL) and divide by the numeric corrective action standard concentrations that are designated for cancer evaluation ("ca").
• Multiply this ratio by 10^{-6} to estimate chemical-specific risk for a reasonable maximum exposure (RME).
• For multiple pollutants, simply add the risk for each chemical:

$$Risk \; = \; [(\frac{conc_x}{PRG_x}) \; + \; (\frac{conc_y}{PRG_y}) \; + \; (\frac{conc_z}{PRG_z})] \; x \; 10^{-6}$$

$$Hazard \; Index \; = \; [(\frac{conc_x}{PRG_x}) \; + \; (\frac{conc_y}{PRG_y}) \; + \; (\frac{conc_z}{PRG_z})]$$

• For non-cancer hazard estimates. Divide the concentration term by its respective non-cancer numeric corrective action standard designated as "nc" and sum the ratios for multiple contaminants.The cumulative ratio represents a non-carcinogenic hazard index (HI). A hazard index of 1 or less

is generally considered "safe". A ratio greater than 1 suggests further evaluation. Note that carcinogens may also have an associated non-cancer numeric corrective action standard listed in table. Where both cancer-based and non-cancer-based standards are listed, appropriate evaluation should be conducted for both standards.

In Tier 2 and 3, all COCs detected may be assessed in a forward, cumulative risk assessment when:

C   >10 carcinogens are identified;

C   >1 Class A carcinogen is identified;

C   any non-carcinogen has a hazard quotient of 1/nth of the hazard index of 1, where n represents the total number of non-carcinogens identified; and

C   >10 non-carcinogens are identified.

The forward risk assessment calculation must demonstrate a hazard index (HI) as the sum of the chemical-specific HQ's of less than 1, and a cumulative ELCR no greater than 10^{-4}.

Tier 2 compliance may be achieved through use of engineering and institutional controls that exceed the AWQSs, but documentation must be provided that natural attenuation is likely to effect compliance with the AWQSs in time. The proper description of acceptable site-specific conditions for remediation by natural attenuation is found in the the ADEQ guidance manual, downloadable on the ADEQ web page (http://www.adeq.state.az.us/environ/waste/ust/cap.html) and in the ASTM Standard Guide (ASTM, 1998b).

6.3.10   Institutional and Engineering Controls

Institutional and engineering controls may be used as part of the Tier 2 or Tier 3 evaluation when eliminating certain exposure pathways or reducing the magnitude of the exposure. Not only must these controls be memorialized in the DEUR, but they must be maintained until such time that the restriction is no longer needed to protect human health and the environment under conditions of typical residential uses. These controls may be applied to both residential as well as non-residential property uses.

Institutional controls are typically those actions which direct limits to receptor behavior or property uses. An example is the operational policy for a correctional facility which houses inmates. Another example is one in which the property is the site of a nursing care facility for geriatric residents. The conceptual site model and the resulting risk assessment would utilize assumptions which are consistent with these designated uses. The factors which drive the need for an institutional control are any behavioral or exposure assumptions which are subject to human influences that are different than the assumptions utilized to construct the Tier 1 risk-based standard.

Engineering controls may be as simple as a physical barrier which must remain in place, *e.g.*, a building or concrete slab, or may be an active treatment system which requires periodic maintenance and replacement, *e.g.*, a wellhead filtration/GAC treatment system.

The UST Program requires execution of the DEUR to the property deed for either type of control in order to ensure implementation of the control and for granting LUST site closure.

6.3.11   TPH, Metals, Chlorinated Compounds, and MTBE

To accomplish a risk-based evaluation for petroleum hydrocarbons, different approaches are available. One approach is to apply toxicity data directly from studies based on the specific petroleum product subject to evaluation. However, toxicity data for specific petroleum types may be lacking. Alternatively, toxicity data may be substituted from studies conducted on a similar fuel type, if available. This presents a disadvantage in regard to the environmental fate and disposition of individual constituents which are dissimilar between the two petroleum product types. Another method utilizes a breakdown of the hydrocarbon fractions that are present in environmental samples and correlates them to those fractions designated by the TPH Criteria Working Group for which a toxicity factor has been assigned (Edwards, et al, 1997). The hydrocarbon fractions should correspond to the working group fractions as follows:

Aliphatic C5-6	Aromatic C5-7
Aliphatic C6-8	Aromatic C7-8
Aliphatic C8-10	Aromatic C8-10
Aliphatic C10-12	Aromatic C10-12
Aliphatic C12-16	Aromatic C12-16
Aliphatic C16-35	Aromatic C16-21

Aromatic C21-35

These are the TPH fractions with toxicity factors that can be used for a risk-based evaluation for non-cancer effects. There are analytical laboratories that conduct aliphatic/aromatic fraction analyses, but the method published by the TPHCWG, called the Direct Method, is not yet an adopted EPA Method. Lastly, the impacts to health from any petroleum contamination may be assessed by the individual constituents present which have established toxicity data. ADEQ only requires that a compelling demonstration of protection of human health and the environment be made for TPH, whatever the method.

In some cases, a crude petroleum fraction or waste oil may be enriched for certain metals such as arsenic, cadmium, chromium, vanadium and nickel. Lead is usually not present unless blended as part of older formulations of automotive fuels. In such cases of releases involving these products at LUST sites, analyses for these metals may be appropriate in soil samples collected from the vertical or source boring, as there presence and concentrations are dependent upon the cation exchange capacity and humic content of soils. If not detected, further delineation for these compounds is not warranted. The evaluation of risk due to metals may utilize the approach for evaluating total metals, or speciation of metals. For example, health risk due to elemental mercury is different from that of methylmercury. Another example is that of chromium, for which the hexavalent state is more toxic than the trivalent state. Lead should be assessed at the Tier 2 and 3 levels using the most recent updated versions of US EPA's IEUBK Model available from their website.

Leaded fuels also containing lead scavengers, 1,2-DCA and/or EDB, should be evaluated in soils only in the source boring for defining vertical extent due to the chemical properties of these compounds. Once these compounds have migrated into groundwater, the greatest evidence of their presence will be in groundwater samples collected at the source and downgradient due to their recalcitrant behavior in the subsurface.

MTBE is specifically discussed in this guidance due to its widespread use as a fuel additive for which a numeric AWQS has not been adopted in Arizona. However, many states have established groundwater remediation and/or action levels for this compound based upon review of the toxicological data currently available. As MTBE is a regulated compound, it, along with all other compounds resulting from a release from a regulated UST system must be addressed in site investigation of soils and in

groundwater. MTBE has an established Tier 1 corrective action standard in soil, *i.e.* Arizona SRL. Calculation of Tier 2 and 3 soil standards should rely upon the most recent scientific, peer-reviewed toxicity and fate/transport data.

With regard to levels of MTBE in groundwater, until the UST Release Reporting and Corrective Action Rule is promulgated, the department has developed a policy for addressing when, how, and to what levels should MTBE be investigated and remediated. This policy closely mirrors the protocol established by the rule (R18-12-263.01) for addressing any COC which has no numeric AWQS but may result in a potential impact to human health (see Appendix Q for policy). Specifically, MTBE should be investigated by delineating the contaminant plume in soil and groundwater to the extent of the most stringent of the potential applicable remediation levels, *i.e.*, GPL, residential SRL, drinking water quality level. However, remediation for MTBE in groundwater should be conducted when a receptor (water supply well) is currently impacted or may potentially be impacted in the future. The groundwater remediation level should be consistent with the more stringent of the values which are protective of human health or protective of the quality of the drinking water. As is the case with several chemicals, the taste/odor threshold for MTBE in water is lower than the risk-based level. Therefore, remediation to the risk-based level is required when no receptor is potential impacted, and remediation to the drinking water quality level is required when a receptor may be potentially impacted. The determination of both the risk-based level and the drinking water quality level should be consistent with the tiered RBCA approach described in this guidance and provided for in rule. Care should be taken to use the most recent and peer-reviewed information receiving consensus among the scientific community and should be well documented for use in tier evaluation reporting.

6.4   TIER 3 EVALUATION

Tier 3 evaluation is the most detailed and focused evaluation allowed in the tiered evaluation process. If the results of Tier 3 evaluation still indicate that remedial action is warranted, then a corrective action corrective plan (CAP) is required to be submitted and approved for that action. The CAP is to describe the corrective action goals in implementing a remedy and may include engineering and institutional controls.

6.4.1 Screening Process for Determining Whether to Proceed with Tier 3 Evaluation

The decision logic and factors for determining whether to proceed with Tier 3 evaluation are the same as those for Tier 2, described in Section 6.3.2. In one respect, proceeding with Tier 3 evaluation rather than proceeding with remedial action is a business decision because remedial action may still be warranted and required after the expense of additional analysis in Tier 3. The decision to proceed with Tier 3 should be thoroughly reviewed among the regulated entity, the participating consultant company, and the ADEQ. ADEQ does not pretend to participate in business decisions but is a valuable resource in scoping whether Tier 3 evaluation might be successful in refining the risk-based analysis and the subsequent decision.

6.4.2 Selection of Appropriate Modeling

The models incorporated in Tiers 1 and 2 are appropriate for those uses because those models are conservative in their relative simplicity. In Tier 3, the desire is for a closer correspondence to site-specific conditions, thereby affecting less conservative evaluation, so more detailed models are appropriate. Several resources exist for selecting appropriate models.

The EPA Center for Subsurface Modeling Support (CSMoS, http://www.epa.gov/ada/csmos.html) has groundwater and vadose zone models and technical support for those models. The EPA Office of Research and Development National Center for Environmental Assessment lists the Integrated Model Evaluation System (IMES, http://www.epa.gov/ncea/imes.htm) as a risk assessment tool. IMES is an interactive system for selecting fate models for air, surface water, groundwater, and multi-media releases. It includes information on over 100 models addressing items such as the input requirements, level of detail, required user expertise, applications, validation and other technical features.

It is distributed on a CD-ROM (Exposure Models Library and Integrated Model Evaluation System, EPA/600/C-92/002, September 1992) that includes many of the fate models themselves and their manuals. IMES is a persuasive tool for describing why a particular model is chosen for Tier 3 analysis.

An important rule of thumb for Tier 3 models is that the more proprietary the model (code privately controlled), the less likely it is to be approved for Tier 3 analysis. This is not to rule out proprietary models, but rather to promote (and require) the common understanding among all stakeholders of the potential results to be obtained from the model and the correspondence of those results to site-specific conditions.

Every new model introduced in the Tier 3 analysis must be acceptable to ADEQ. It may be appropriate for Tier 3 analysis incorporating less familiar models to prepare a Tier 3 risk assessment work plan and to present it in meeting with ADEQ. This provides opportunity to understand the algorithms, the site-specific inputs, and the results that may be presented in the Tier 3 risk assessment report.

6.4.3 Additional Site-Specific Data Requirements

Additional site-specific data are crucial for Tier 3 evaluation. Tier 1 was based on look-up concentrations based on conservative, standardized site conditions. Tier 2 allowed incorporation of some site-specific information, usually readily available, to modify parameters in conservative models. Tier 3 provides the opportunity to obtain the best characterization of COC conconcentrations and site-specific geotechnical parameters for the most realistic characterization of the release. Therefore, data requirements for Tier 3 should include any and all data that support more site-specific, realistic evaluations to the extent that models can correspond to site-specific conditions. An effective tool for communicating the intent and structure of the Tier 3 evaluation is to submit a work plan to ADEQ for the Tier 3 mobilization and field investigation. The geotechnical parameters of most importance are listed in the next section.

6.4.4 Selection of Input Parameters (Sensitivity Analysis)

The best tabulation for parameter sensitivity on corrective action standards of various geotechnical parameters is found in the course materials of the ASTM course, "Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites." Since at least one professional from each

consulting company submitting risk assessments under the corrective action rules is to have been RBCA-trained, access to this document should be common. The following listing in Table 6.4.4.a is abstracted from that document as an indicator, but not a substitute, for the information therein.

Table 6.4.4.a ASTM Summary of Parameter Sensitivity for Modeling

Parameter Change Influence on Risk-Based Concentrations	
Parameter	**Pathway(s) Affected**
Soil Parameters	
Bulk density	All
Fraction of organic carbon	All
Total porosity	All
Volumetric water content in vadose zone	All (not used in dilution-attenuation factor [DAF] calculation)
Volumetric air content in vadose zone	All (not used in DAF calculation)
Thickness of capillary fringe	Groundwater volatilization to indoor air Groundwater volatilization to outdoor air
Volumetric water content in capillary fringe	Groundwater volatilization to indoor air Groundwater volatilization to outdoor air
Volumentric air content in capillary fringe	Groundwater volatilization to indoor air Groundwater volatilization to outdoor air
Groundwater Parameters	
Depth to groundwater	Groundwater volatilization to indoor air Groundwater volatilization to outdoor air
Infiltration rate of water through soil	Subsurface soil leaching to groundwater
Groundwater Darcy Velocity (calculated using hydraulic conductivity and hydraulic gradient)	Subsurface soil leaching to groundwater (also used to estimate DAF)
Groundwater mixing zone height	Subsurface soil leaching to groundwater
Air Parameters	
Wind speed above ground surface in ambient mixing zone	Groundwater volatilization to outdoor air Subsurface soil volatilization to outdoor air Surface soil volatilization/particulate emission to outdoor air

Ambient air mixing zone height	Groundwater volatilization to outdoor air Subsurface soil volatilization to outdoor air Surface soil volatilization/particulate emission to outdoor air
Particulate emission rate	Surface soil volatilization/particulate emission to outdoor air
Source Parameters	
Width of source area parallel to wind/groundwater flow	Groundwater volatilization to outdoor air Subsurface soil volatilization to outdoor air Surface soil volatilization/particulate emission to outdoor air Subsurface soil leaching to groundwater
Depth to subsurface soil sources	Subsurface soil volatilization to outdoor air Subsurface soil volatilization to indoor air
Lower depth of affected surficial soil zone	Surface soil volatilization/particulate emission to outdoor air
Building Parameters	
Enclosed-space air exchange rate	Groundwater volatilizaton to indoor air Subsurface soil volatilization to indoor air
Enclosed-space foundation/wall thickness	Groundwater volatilization to indoor air Subsurface soil volatilization to indoor air
Enclosed-space volume/infiltration area ratio (This parameter relates the volum of the basement to the depth of the basement below ground surface (bgs)	Groundwater volatilization to indoor air Subsurface soil volatilization to indoor air
Areal fraction of cracks in foundation/walls	Groundwater volatilization to indoor air Subsurface soil volatilization to indoor air
Volumetric air content in foundation/wall cracks	Groundwater volatilization to indoor air Subsurface soil volatilization to indoor air
Volumetric water content in foundation/wall cracks	Groundwater volatilization to indoor air Subsurface soil volatilization to indoor air
Abstracted from sensitivity tables in course materials of ASTM course, "Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites."	

Depending on the pathways applicable for the release and the site, selected site-specific parameter characterization, especially for sensitive parameters, is warranted. The risk assessment report should describe the source of site-specific parameters and/or the methodology for measuring those parameters invoked in the models of Tier 3.

6.4.5 Revising the CSM

The final CSM resulting from the Tier 3 evaluation should document the exposure pathways that are 1) incomplete, 2) have insignificant impact (risk-based), and 3) are designated for remedial action. A site-specific description of the rationale for all pathway decisions must be included in the report.

The CSM shown in Figure 6-1 herein and Figures 2, X5.1, and X5.2 of ASTM, 1995 present ways to indicate on the final CSM the complete pathways, incomplete pathways, and remedial actions based on engineering and institutional controls appropriate to controlling risk. Those interested in a standard software package for generating CSMs are referred to *http://tis-nt.eh.doe.gov/oepa/programs/scem.cfm*. The executable file is called the *Site Conceptual Exposure Model (SCEM) Builder* (DOE, 1997).

6.4.6 Determining the Point of Compliance

The primary "driver" for determining the point of compliance is Arizona law. For instance, the version (1996) of the Arizona GPL (Groundwater Protection Level) software currently in use incorporates a point of compliance (POC) that is 100 feet downgradient from the point at which soil leachate reaches and mixes with the groundwater. However, current Arizona law requires the protection of the groundwater at the point at which soil leachate reaches groundwater. Therefore, levels of COCs in soil may not leach to the extent which results in the exceedance of the AWQSs. The POC is the vertical soil column which results in levels exceeding the AWQS at all locations of contact and mixing with the groundwater.

The POC for groundwater contamination at the Tier 3 level may occur beyond the nearest downgradient property boundary when off-site conditions result in no exceedance of the AWQSs at the existing point of use. To be protective of future groundwater uses, assurances must be documented in the CAP which demonstrate that levels of COCs in groundwater will not result in an exceedance of the AWQS at the **time** of use. This may require the use of a DEUR which includes restricting groundwater end uses, preventing the installation of wells, or requiring specific well construction and screened interval in the saturated zone of the subsurface. This allows by law [A.R.S. § 49-1005(E)] the exceedance of the AWQS while maintaining the protection of human health and the environment until such time that the AWQS may be achieved by the remedial alternative selected in the approved CAP.

For soil-related pathways, Arizona law requires compliance with SRLs anywhere on a property as if there were a human receptor located there. The receptor survey described in Section 6.1.1 helps to substantiate the likely receptors and land use of the site to designate the POC for incidental ingestion exposure to soil. Where soil may be transported to a remote location by volatilization and/or fugitive dust entrainment in air, the POC for that pathway is at the location of the exposure. In the absence of criteria for fugitive dust exposure, as with SRLs, the risk-based evaluation incorporating wind roses, modeling, and risk-based evaluation helps to establish the location of maximum exposure, the POC.

6.4.7 Determining Representative Concentrations for COCs

Representative concentrations in Tier 3 should be more refined than in Tier 2. Site-specific data, including geotechnical parameters should be more precise and the evaluation should benefit from it. Specifically, the statistical evaluation described in Section 6.3.3 (Site-Specific Data and Data Requirements) pertained to what can be thought of as essentially a two-dimensional expanse across an area(s) of the site, with a depth for the COC contamination based on the limited number of borings in Tiers 1 and 2. With additional site characterization in Tier 3, it is appropriate to represent COC concentrations as a three-dimensional array of surface and subsurface COC concentrations based on the increase in data. The refinement of the COC distribution, alone, could justify reducing remedial action (and remediation costs) substantially.

For sites with heavy petroleum use, as at large distribution facilities, it is appropriate to confirm that certain areas are not part of the AOC. In that regard, the additional site characterization and refinement of the AOC boundaries should be empahsized in the risk assessment report as confirmation of the areas that do not require further attention.

6.4.8 Comparison of Tier 3 Corrective Action Standard with Site Contamination

The methodology of Section 6.3.9 also applies in Tier 3. Comparison of representative COC concentrations to site-specific corrective action standards will be conducted. Cumulative risk/hazard must also be determined to demonstrate that additive effects from the COCs are not a concern. Comparison to risk-based standards and determination of chemical-specific risk/hazard must be conducted for each AOC and for each complete exposure pathway.

Comparison of media-specific concentrations of MTBE to site-specific corrective action standards must be consistent with ADEQ's *Report on Methyl Tertiary Butyl Ether (MTBE)*, October 1, 1999, and pertinent updates.

6.4.9 Institutional and Engineering Controls

Unless a remedial action will remove completely the threat associated with an environmental release, the remedy for that release will include both engineering and institutional controls. However, the prudent application of risk-based criteria with assurance that natural attenuation processes will continue in the future can provide a proper basis for closure.

The presence of persistent COCs such as MTBE and PNAs may require additional consideration. For instance, MTBE in groundwater with nearby potential exposure receptors may necessitate monitoring beyond the time for closure with respect to petroleum hydrocarbons. In such case, a DEUR will be required, including the commitment to conduct and report the monitoring for the protection of potential human receptors. If selected exposure pathways are declared incomplete because of site-specific features, such as landscaping to cover soil, fences to restrict access, or concrete/asphalt covering of soil, a DEUR will be required in the event that those facilities are removed. The potential for institutional controls as part of the final remedy should be communicated to ADEQ as part of the strategy for the characterization and remedial action on the site.

6.4.10   Preparation of the Tier 3 Evaluation Report

The Tier 3 evaluation report is unique because it represents the best, most detailed analysis that is appropriate to the environmental investigation and characterization of the site. For most UST sites, there should not be need for Tier 3 analysis. However, for complicated exposure circumstances, such as off-site groundwater contamination presenting exposure potential to large populations, for instance, it may be appropriate to conduct a Tier 3 evaluation.

The Tier 3 evaluation is also unique because it allows the flexibility to incorporate models and site-specific information not yet included in the Tier 1 or 2 evaluations. That carries with it the responsibility to provide a thorough explanation of the basis, validity, conservatism, and sensitivity of the model(s) chosen that differ from those provided by ADEQ in Tier 1 or 2.

A good motto for preparing and submitting the Tier 3 risk assessment report is... **No surprises for any of the stakeholders**. This objective will be met

by thorough communication with ADEQ during risk assessment development and adhering closely to the procedures contained in this guidance.